The Nature of the αβ-Process in Palladium-catalysed Multiple Exchange Reactions of Polycyclic Hydrocarbons with Deuterium: Significance of Bridgehead Olefin Stability

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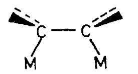
Summary The ease with which multiple exchange reactions of polycyclic hydrocarbons with deuterium, catalysed by palladium, propagate through bridgehead positions is related to the stability of the appropriate bridgehead olefin, indicating that the $\alpha\beta$-process in exchange involves interconversion of a σ-bonded metal alkyl and a π-bonded metal alkene.

Burwell[1] maintains that the $\alpha\beta$-process for exchange of alkanes with deuterium on metals is the interconversion of monoadsorbed alkyl with eclipsed 1,2-diadsorbed alkane (**1**). We now present results which strongly support the view that the 1,2-diadsorbed species is π-bonded alkene (**2**).[2]



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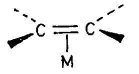

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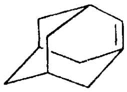

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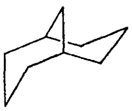

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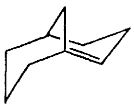

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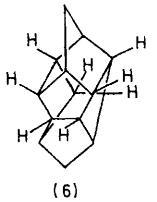

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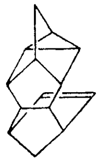

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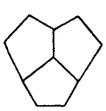

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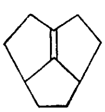

(9)

Exchange reactions with acyclic and monocyclic alkanes cannot provide a distinction between the two descriptions, nor can most bicyclic and tricyclic alkanes. For example, adamantane undergoes only simple exchange with deuterium on palladium,[1] but the rigidity of the adamantane skeleton precludes formation of an eclipsed **1**,**2**-diadsorbed species, and π-bonded adamantene (**3**) is extremely unlikely, even though there is evidence that in olefin complexes in which the metal is zerovalent (as is a metal surface) there may be some deviation from planarity and multiple bond lengthening as compared with the geometry of the free olefin.[3] Bicyclo[3,3,1]nonane, a structure closely related to adamantane, readily undergoes multiple exchange through the bridgehead positions.[4] However, the essential eclipsed conformation, involving the bridgehead position, is present in the chair–boat form (**4**), and bicyclo[3,3,1]non-1-ene (**5**) is a moderately stable olefin.[5]

The tetradecane (**6**),[6,7] prepared conveniently in quantitative yield by passing the norbornadiene dimer (**7**) in nitrogen over an activated silica–alumina catalyst at 300°, possesses four separate pairs of perfectly eclipsed vicinal tertiary hydrogens out of a total of 16. Burwell's mechanism predicts that compound (**6**) should show multiple exchange with deuterium on palladium in a manner very similar to that of bicyclo[2,2,1]heptane which yields initial exchange of two hydrogen atoms (mainly on C-2 and C-3) at 75° with a $^2H_2/^2H_1$ isomer ratio of *ca.* 2. Models imply that to incorporate a double bond into (**6**) would produce a system so highly strained that there should be only a remote possibility of forming a π-complexed olefin on the metal. Our mechanism predicts that there should be simple exchange only.

Exchange reactions of (**6**) in excess of deuterium at different temperatures and conversions were carried out on a 2% w/w $Pd-\gamma-Al_2O_3$ catalyst. If simple stepwise exchange occurs the experimental distribution of deuterio-isomers should agree closely with that calculated on the basis of 16 exchangeable hydrogens using the binomial theory. This was indeed the case for all experiments, two of which are summarised in the Table. These results fully support our mechanism and reinforce the contention that reactions of hydrocarbons catalysed by metal surfaces, *e.g.* hydrogenation, have much in common mechanistically with the same reactions catalysed homogeneously by transition-metal complexes.

Table

Observed (*A*) *and calculated* (*B*) *distributions of deuterio-isomers*

	T/°C	$^2H_0$	$^2H_1$	$^2H_2$	$^2H_3$	$^2H_4$	$^2H_5$
A	80	74·9	21·1	3·7	0·3	—	—
B	80	74·3	22·3	3·1	0·3	—	—
A	90	49·5	33·0	13·4	3·3	0·6	0·2
B	90	47·3	36·3	13·0	2·9	0·5	0·1

It should now be possible to predict qualitatively bridgehead olefin stabilities from experimental deuterium exchange distributions. We have found, for example, that the tricyclodecane (**8**)[8] initially exchanges 10 hydrogen atoms (presumably those on the convex surface) with the following distribution at 92° on palladium: $^2H_0$ 79·6, $^2H_1$ 4·5, $^2H_2$ 2·2, $^2H_3$ 1·6, $^2H_4$ 1·8, $^2H_5$ 1·7, $^2H_6$ 1·6, $^2H_7$ 1·7, $^2H_8$ 1·5, $^2H_9$ 1·6, and $^2H_{10}$ 2·3. On this basis we may predict that olefin (**9**) (presently unknown) should be a compound of moderate stability.

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